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MIKIO SHIMIZU

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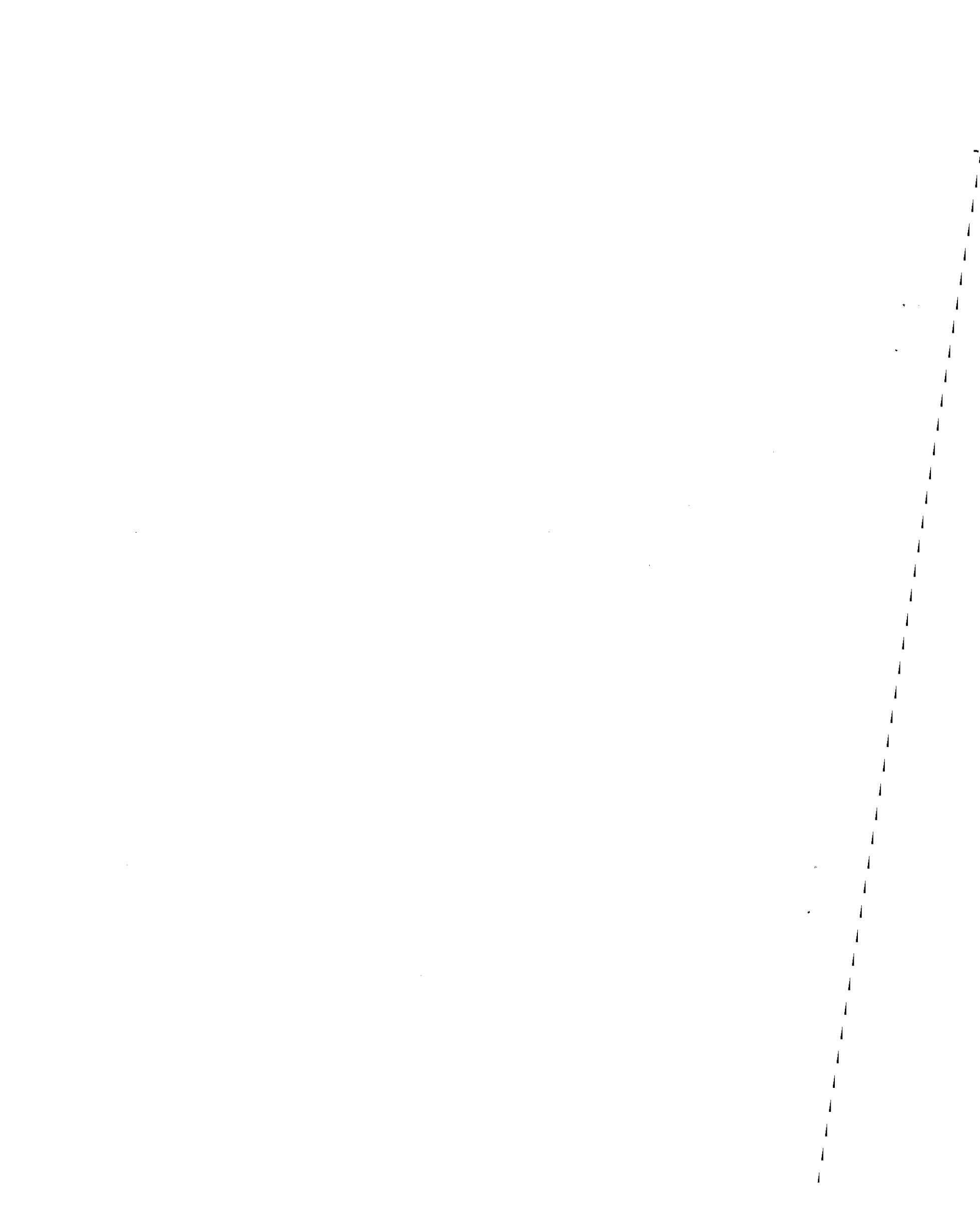


A DISCUSSION OF CO AND O ON VENUS AND MARS

by

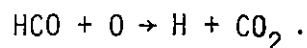
Mikio Shimizu*
Laboratory for Planetary Atmospheres
Goddard Space Flight Center
Greenbelt, Maryland

* NAS-NRC Senior Research Associate, on leave from ISAS, The
University of Tokyo

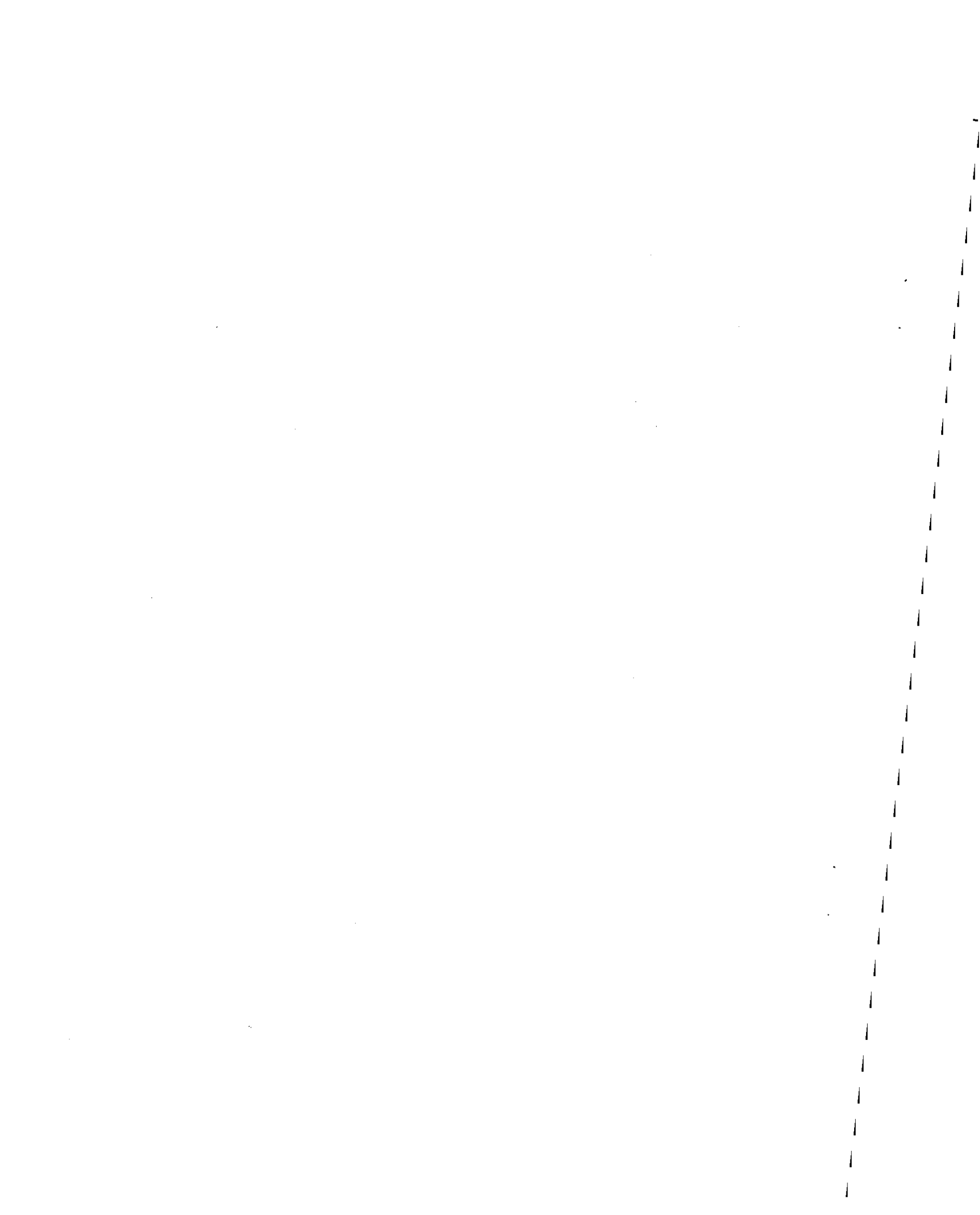


ABSTRACT

The absorption of solar ultraviolet radiation in the wavelength range 2000 - 2200 Å by CO₂ strongly reduces the dissociation rate of HCl on Venus. The Cl catalytic reaction for the rapid recombination of O and CO and the yellow coloration of the Venus haze by OCl⁻ and Cl₃⁻ appears to be unlikely. At the time of the Martian dust storm, the dissociation of H₂O in the vicinity of the surface may vanish. The increase of dissociation at high altitudes, however, can be the source of H atoms in the upper atmosphere. H atoms from the dissociation of hydrides may catalyze the recombination of CO and O in the lower atmospheres of these planets according to the following scheme:



In the case of Venus, there may be other kinds of sinks for the photodissociation products, and its chemical environment might be more complex than that of Mars.

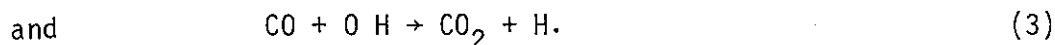


1. INTRODUCTION

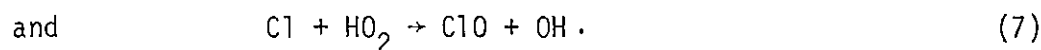
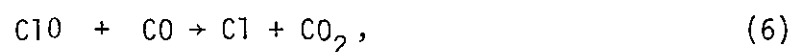
The scantiness of CO and O in the upper atmospheres of Venus and Mars found by planetary probes such as Mariners and Veneras appears to be best explained by the dilution of these chemical species due to atmospheric mixing (Shimizu, 1968, 1969, 1971, and 1972; Shimazaki and Shimizu 1970, Dickinson, 1971; Shimizu and Ashihara, 1972). There is no known chemical reaction to remove the photodissociation products of CO₂ fast enough to provide a concentration as low as that observed (Clark, 1971). The hydrogen-deuterium hypothesis (Donahue, 1969a, McElroy and Hunten, 1969) which restricted the magnitude of turbulent mixing coefficient to very low values should be abandoned on the basis of recent sounding rocket experiments (Donahue, 1971).

On the other hand, the neutral photochemistry in the lower atmospheres of Venus and Mars are not yet well understood. A comparison of the known three body loss rate between O atoms and that between O and CO shows that O (³P) atoms transported from the upper atmosphere or produced directly at lower altitudes may recombine to form O₂ rather than CO₂. The observed amounts of O₂ and CO on these planets are, however, extremely small: CO/CO₂ are 4×10^{-5} and 10^{-3} , respectively (Connes et. al., 1968; Kaplan, et. al., 1969), and O₂/CO₂ are 4×10^{-6} and 2×10^{-3} , respectively (Carleton and Traub, 1972; Barker, 1972), on Venus and Mars.

Reeves, et. al., (1966) pointed out that water may play a role as a catalyst for the rapid recombination between CO and O. Donahue (1969b) suggested the following chain mechanism:



The reaction (2) was shown later to be extremely slow (Baldwin et. al., 1970). Prinn (1971) proposed a catalytic reaction by Cl (for Venus only):



As we shall discuss later, the dissociation rate of HCl to form Cl is much smaller than Prinn expected. We shall suggest a chain reaction involving HCO which might partly explain the scantiness of CO and O₂ on these planets.

2. DISSOCIATION OF ATMOSPHERIC CONSTITUENTS ON VENUS AND MARS

2.1 Venus

The Venusian atmosphere seems to be mainly composed of CO₂, with some minor constituents such as CO, O₂, H₂O, HCl, and HF. The amount of H₂O may be variable with time and location, the mean of which is taken here to be 30μ precipitable water. The mixing ratio of HCl is

7×10^{-7} . Prinn (1971) calculated the dissociation rates of these constituents by using the solar UV flux from Schultz and Holland (1963), the photo absorption cross-section compiled by Schultz et al., (1963), and the atmospheric model of Johnson (1968). He concluded that the dissociation rate of HCl in the vicinity of the cloud tops predominated over other rates. In this computation, however, he assumed that CO_2 might be dissociated by the radiation with the wavelengths shorter than 1975 \AA . CO_2 can be dissociated at longer wavelengths. Recently, Ogawa (1971) measured the dissociation cross-section up to 2160 \AA . Since the solar spectrum in this energy region increases sharply towards longer wavelengths, the inclusion of absorption in the 2000 \AA range should result in a considerable change from his conclusion. We computed the dissociation rates of the atmospheric components by using data from the following sources: The solar UV flux by Detweiler et al. (1961) divided by a factor of 3 according to the suggestion of Hinteregger (1970), CO_2 and O_2 cross-section by Ogawa (1971), that of HCl by Romand and Vodar (1948); that of H_2O by Watanabe and Zelikoff (1953), and the atmospheric model from the further analysis of Mariner and Venera data by Ainsworth and Herman (1972). We have plotted the results in Figure 1. The solid lines show the result in which the CO_2 dissociation at wavelengths longer than 2000 \AA is fully taken into account and the dotted curves show the result for the CO_2 cross-sections at wavelengths shorter than 1975 \AA . Above the top of the haze whose location is taken to be 82km in our model, our dissociation rates do not differ much from Prinn's rates.

Below 82km, however, the difference is appreciable. For instance, the dissociation rate of HCl at the cloud top (56km above the surface) is reduced by more than two orders of magnitude due to the shielding effects of CO₂. Above the top of the haze, the dissociation of H₂O might be dominant. Prinn discussed that the cyclic reaction (4) ~ (6) might lead to a fast recombination of O₂ with CO in the lower atmosphere of Venus. The above-mentioned strong shielding effect of CO₂ makes this conclusion seem unlikely. It should also be noted that ClOO is a hypothetical molecule which has not been observed directly in the laboratory. Prinn also suggested that a slight yellow coloration of Venus visible haze might be due to OCl⁻ and Cl₃⁻ ions which are ultimately attributed to the existence of Cl atoms. This suggestion was recently used by Lewis (1972) in the discussion of the Venus haze, but a more careful examination might now be necessary.

2.2 Mars

The Mariner 9 IRIS Experiment has already provided and will continue to provide vertical temperature profiles and water content of the Martian atmosphere for various conditions. At the time of the dust storm, the atmospheric temperature at midlatitude was much higher than that at the time of Mariner 6 observation (Rasool et al., 1970). As the atmosphere became clear, it gradually approached the cooler Mariner 6 temperature (V. Kunde, a private communication). Except within the polar cap region water appears to be widely distributed over the planet in the amount of about 10 - 20μ precipitable water (V. Kunde, *ibid*).

We shall take the observed temperature profile at revolution 92 of Mariner 9 as an example for the time of dust storm and the temperature profile derived from it by subtracting 30°K at each altitude (which is almost the same as the Mariner 6 profile) as a typical one at the time of clearing. We assume that H_2O/CO_2 ratio is about 3×10^{-4} on the basis of the Mariner 9 observation. At some altitude, this ratio reaches the saturation mixing ratio. In such a case, by assuming that condensation occurs at once, we shall adopt the latter ratio to derive the vertical distribution of H_2O . In this computation, the day-night average was taken and the solar zenith was set to be 60°.

The calculated dissociation rates of CO_2 , O_2 , and H_2O in such atmospheric models are shown in Figure 2, together with the adopted temperature profiles. Also plotted in the figure is the dissociation rate of H_2O calculated by Hunten and McElroy (1970) with the temperature profile obtained by Gierasch and Goody (1968) that has been adopted by Hunten and McElroy in their computation.

The agreement of our curve at the time of clearing with Hunten-McElroy's is rather good in the lower part of the atmosphere, if we take into account the difference of the adopted temperature profiles and the "arbitrary distribution of H_2O in the bottom 10km" in their calculation. The increase of our curve at 40-50km level is due to the isothermal character of the observed temperature profile. Above 50km where no observational data is available, the temperature may decrease towards the mesopause and the dissociation rates also decreases with increasing altitude in the same region. Therefore, we may expect a

maximum of the dissociation rate in this region, which is, however, two orders of magnitude smaller than the rate at the surface.

At the time of the dust storm, the situation is rather different. The ultraviolet radiation may not penetrate to the surface but instead may be absorbed or reflected at the top of the dust cloud. (The dotted line at the bottom of the curve shows this situation). However, the dissociation rate of H_2O at high altitudes is quite high, because the atmospheric temperature is much higher and the saturation pressure of H_2O is much higher than that of the days of clearing. The integrated dissociation rates of H_2O in the two cases are comparable. The second peak at the altitude of 40-50km may be an important source of H atoms in the upper atmosphere at the time of the dust storm.

3. HCO CATALYTIC REACTION

As shown in the preceding section, the dissociation rate of H_2O is the dominant one among the minor atmospheric constituents. Consequently, we may expect the existence of sufficient amounts of H to work as a catalyst in the recombination reaction between CO and O in the lower atmospheres of Venus and Mars. It is well known that a trace of H_2O prevents the dissociation of CO_2 in laboratory experiments. This is a strong support for the rapid recombination mechanism on these planets by virtue of gaseous catalytic reaction involving H atoms.

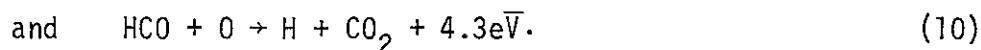
The previous H catalyst theories always used the reaction (3), $CO + OH \rightarrow CO_2 + H$, in their cyclic processes. The following reaction (8) has, however, a greater rate constant by two orders of magnitude

than that of the reaction (3);



Therefore, even if the stationary concentration of O atoms in the lower atmosphere is smaller by two orders of magnitude than that of CO, the reaction rates of (3) and (8) are comparable and the O₂ concentration may go over the observational limits.

In order to avoid this difficulty, we suggest that the following reaction may occur in the lower atmospheres of these planets:



The reaction rates of both processes have not yet been measured. We might expect that the former may be of the order of $10^{-31} \text{ cm}^{-6} \text{ sec}^{-1}$, in analogy with the three body recombination of H with O₂ and NO and that the latter may be as great as or even greater than $10^{-12} \text{ cm}^{-3} \text{ sec}^{-1}$. There is evidence that HCO is not a hypothetical molecule. High dispersion spectra of gaseous HCO have been observed in 4500-7500 Å (Herzberg and Ramsey, 1955). Vibrational bands of HCO in solid matrix was also detected by Ewig et al., (1960). Microwave spectra of this molecule are now being studied in detail in correlation with the interstellar matter.

A tentative correlation diagram showing the observed states and their probable dissociation products of HCO is given in Figure 3. The observed pre-dissociation phenomena which start at 1.54 eV above the

ground state level may be explained by the crossing of the repulsive $^2A'$ state with the first excited $^2A''\pi$ state (Johns, Priddle, and Ramsey, 1963). Due to the crossing between two $^2A'$ states, the ground state combination $H(^2S) + CO(^1\Sigma^+)$ might smoothly connect with the ground state $^2A'$ of HCO. The details of the energy curves at the crossing points are unknown and should be very complex, because of the fact that polyatomic molecules have more degrees of freedom than diatomic molecules (Teller, 1937). A route from $H(^2S) + CO(^1\Sigma^+)$ to the ground state of HCO without any barrier may be possible along some coordinate. Even if a small barrier exists in the vicinity of the crossing point, the depression of the barrier may occur by the formation of the reaction complex of CO with the third body in the case of three body recombination. The third body will carry away all the excess energy to form HCO after the collision of H atoms.

The lifetime of HCO may be short due to the predissociation after the absorption of visible radiation. (Short life times are also claimed for the cases of ClO_2 and CO_3 catalytic reactions). The reaction time for the process (10) may, however, be shorter than this: By assuming the usual dissociation cross-section 10^{-18} cm^2 for HCO and by using the observed solar radiation fluxes in visible and near infrared region (Landolt-Börnstein Table, 1965), the life time of HCO may be of the order of 10^{-4} sec . Therefore, if the reaction rate constant of the process (10) is assumed to be $10^{-12} \text{ cm}^3 \text{ sec}^{-1}$, the O concentration should be more than 10^8 cm^{-3} at the recombination level, to compete with the dissociation rate. The analysis of 1304 Å airglow of Mariner 6

gave the O density of the order of 10^9 cm^{-3} at the peak of electron density profile (Thomas, 1971). The density at the lower altitude is probably higher. In the case of Venus, Rottman and Moos (1972) observed a larger amount of O atoms in its upper atmosphere than on Mars. Consequently, if the reaction rate of the process (10) is as rapid as $10^{-12} \text{ cm}^{-3} \text{ sec}^{-1}$, the instability of HCO to solar radiation may not be serious for our discussion.

In the case of reaction (2), $\text{HO}_2 + \text{CO} \rightarrow \text{OH} + \text{CO}_2$, the effect of steric hindrance can be large, which ultimately may increase the activation energy of this reaction to a large value. The reaction (10) eases this difficulty, because the O atom has no directional bias.

4. FURTHER REMARKS ON CO AND O₂

Although the catalytic reactions (9) and (10) might recombine most of O and CO rapidly, a part of O will convert to O₂ through other rapid processes such as the reaction (8) and so on. Dissociation of CO₂ produces O₂ and CO in the ratio of 1:2. In the case of Mars, the observed amounts of O₂ and CO are 10 cm atm. and 6 cm atm., respectively. 7 cm atm. of O₂ might ultimately come from the dissociation of H₂O, followed by the escape of H atoms from the exosphere. On Venus, on the other hand, they are about 1 cm atm. and 13 cm atm., respectively. Lewis (1969) computed the abundance of atmospheric gases in thermochemical equilibrium with the lithosphere of Venus, and concluded that oxygen has negligible abundance and that the H₂/CO₂ ratio is about 10^{-6} . If we use this result, 2 cm atm. of CO and 1 cm atm. of O₂ may reflect the photochemical situation in the upper part of the Venusian atmosphere and 11 cm atm. of CO that is in the vicinity of the cloud tops at 56 km altitude.

Lewis assumed complete mixing of the atmosphere. The atmospheric circulation in the lower part of Venusian atmosphere might however, be very slow and this assumption may be permissible only in the close vicinity of the surface. Cloud particles may play the role of the catalyst to establish thermochemical equilibrium among the atmospheric constituents. Consequently, it may be instructive to conduct a thermochemical calculation at some levels of the cloud layer to find the thermally stable components. The initial ratios of H, C, and O are assumed to be the same as that derived from the observed amounts of CO_2 , O_2 , CO, and H_2O . The abundance of CO_2 , O_2 , CO, H_2O , OH, and H_2 in equilibrium are roughly estimated. The result shows (1) that the concentration of O_2 is still negligible at the atmospheric level where the temperature is 300°K (about 50 km above the surface), and (2) that below this level, the amount of H_2O is overwhelmingly greater than that of H_2 . This means that there can be a thermal sink of O_2 and H_2 at 40-50km level.

Another possibility for the role of cloud particles is that they are substances that react with some of the gases such as H_2 , O_2 , and CO. In such a case, the thick cloud can be the sink of the atmospheric constituents.

These considerations suggest that, in the case of Venus, there might be various kinds of sinks for the photo-dissociation products at the cloud and haze levels. Indeed, the escape flux of H atoms from the exosphere of Mars derived from observations is of the same order of or a

little smaller than the integrated H production rate in the lower atmosphere (Anderson and Hord, 1971), while the escape flux on Venus is much smaller than the integrated production rate, say by three orders of magnitude. This may reflect the chemical condition discussed above. The photochemistry of the Venus atmosphere might be more complex than that of Mars.

5. SUMMARY

The dissociation rate of HCl on Venus may be much smaller than the value previously discussed by Prinn (1971), if we include the strong shielding effect of CO_2 in the 2000-2200 Å wavelength range which has not been taken into account in his calculation. The dissociation of H_2O in the vicinity of the Martian surface will vanish at the time of the dust storm by the absorption or reflection of the solar UV radiation at the dust cloud top. However, the dissociation at high altitudes will be increased at this time, due to the higher atmospheric temperature. H atoms in the upper atmosphere will be directly supplied from this source. Since the production rate of H atoms is appreciable in the lower atmospheres of Venus and Mars, the rapid recombination of CO and O might there be catalyzed by these atoms. A cyclic scheme including HCO which is actually detected by many investigators in the laboratory is suggested to explain the scantiness of CO and O_2 on Venus and Mars.

It may be premature to conduct a quantitative theoretical study on the chemical processes in the lower atmosphere of Venus and Mars, because of many ambiguities concerning the physical and chemical conditions of

the Venus clouds and the Martian surface. The measurements of the rate constant for the reactions (9) and (10) in the laboratory, however, are urgently needed.

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FIGURE CAPTIONS

Figure 1 - The Molecular Dissociation rates of various atmospheric constituents on Venus: solid lines show the results in which the dissociation of CO_2 in 2000-2200 Å region is fully taken into account. Dotted lines are for those in which it is neglected.

Figure 2 - The molecular dissociation rates of various Martian atmospheric constituents. The rates of H_2O are calculated for two temperature profiles plotted at the left hand. The result obtained by Hunten and McElroy on the basis of the temperature profile of Gierasch and Goody is also shown in the figure.

Figure 3 - The correlation diagram of the observed states and their probable dissociation products of HCO. The energy level for the ground state combination of CO and H is assumed to be higher than the ground state level of HCO by 1.2eV , the probable dissociation energy of HCO.

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